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Liquid coating composition and method for forming a fluorine-doped tin oxide coating on glass.

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Abstract

A fluorine-doped tin oxide coating is formed on glass using an organotin di- or tri-carboxylate with an organic fluoroacid. About 50-80% organotin compound and 20-50%. fluoroacid are used, applied in vaporised form to the heated glass surface. The resulting coatings have low bulk resistivities and Gardner haze values. The preferred compounds used are dibutyltin diacetate and trifluoracetic acid.

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(54) **Liquid coating composition and method for forming a fluorine-doped tin oxide coating on glass.**

(57) A fluorine-doped tin oxide coating is formed on glass using an organotin di- or tri-carboxylate with an organic fluoroacid. About 50-80% organotin compound and 20-50%. fluoroacid are used, applied in vaporised form to the heated glass surface. The resulting coatings have low bulk resistivities and Gardner haze values. The preferred compounds used are dibutyltin diacetate and trifluoracetic acid.

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LIQUID COATING COMPOSITION AND METHOD FOR FORMING A FLUORINE-DOPED TIN OXIDE COATING ON GLASS

This invention relates to doped tin oxide coatings on glass, and more particularly, to a composition and method for forming fluorine-doped tin oxide coatings on glass, as well to coatings thus formed having improved electrical and haze properties.

Belanger et al in the J. Can. Cer. Soc. 52, 28-32 (1983), and the J. Electrochem. Soc. 32, 1398-1405 (1985), describes a method of forming Sb-doped tin oxide films on glass substrates by chemical vapor deposition of dibutyltin diacetate with antimony (V) chloride ($SbCl_5$) or trichlorotrifluoroethane (CCl_3-CF_3) as dopants in an oxidizing atmosphere using nitrogen as a carrier gas at substrate temperatures of 420-450° C. These Sb-doped films, however, have relatively high bulk resistivities of greater than 1×10^{-3} ohm-cm.

Abe, et al JP 61,188,821, issued Aug. 22, 1986, describes a method of preparing fluorine-doped tin oxide coatings using trifluoroacetic acid as the dopant in 25-65 wt. % of trichloroethane as a solvent. However, relatively poor bulk resistivities of 10^{-3} ohm-cm. are obtained.

So, the problem addressed herein is to provide a new composition and method for making fluorine-doped tin oxide coatings on glass,which preferably have bulk resistivities of the order of 10^{-4}ohm-cm., and reduced haze.

One aspect of the solution given by the invention is to provide a liquid coating composition including an organotin di- or tricarboxylate and an organic fluoroacid, from which a fluorine-doped tin oxide coating of predetermined thickness having excellent bulk resistivities and haze values may be made by chemical vapor deposition onto glass substrates.

In a preferred version, the invention provides a liquid coating composition comprising dibutyltin diacetate and trifluoroacetic acid, from which a fluorine-doped tin oxide coating of about 2000 A thickness can be made by chemical vapor deposition onto glass substrate having a bulk resistivity of about 10^{-4} ohm-cm., a Gardner haze value of <1%, a visible transmittance of >80%, and an infrared reflectivity of >65%.

The liquid coating composition of the invention comprises about 50-80% by wt. of an organotin di- or tricarboxylate and about 20-50% by wt. of an organic fluoroacid. In the preferred form of the invention, the liquid coating composition includes about 50-60% by wt. of dibutyltin diacetate and about 40-50% by wt. of trifluoroacetic acid.

The method of the invention comprises vaporizing the liquid coating composition, transporting the vaporized coating composition in a carrier gas to a heated glass substrate, and contacting the glass with the vapor composition to deposit fluorine-doped tin oxide coatings on the glass. Such coatings of predetermined thickness have been found to have improved bulk resistivity and haze values.

Preferred organotin compounds of the liquid coating composition can be represented by the general formula:

$R^{1}_{x}Sn(O_2CR^{11})_{4-x}$

where R^1 is a C_1 to C_4 straight or branched chain alkyl or $R^{111}CH_2CH_2$ - where R^{111} is $R^{1V}O_2C$ or CH_3CO and R^{IV} is C_1 to C_4 alkyl; R^{11} is C_1 to C_4 straight or branched chain alkyl; and x is 1 or 2.

Illustrative non-limiting examples of organotin compounds suitable for use herein are: dibutyltin diacetate, butyltin triacetate, methyltin triacetate, dimethyltin diacetate, dibutyltin dipropionate, dimethyltin dipropionate, methyltin tripropionate, diisobutyltin diacetate, bis(carbomethoxyethyl)tin diacetate, and bis(3-oxobutyl)tin diacetate.

The organofluoroacid dopants suitable for use in this invention are reactive fluorine compounds which are strong acids or compounds which have boiling points below 250° C. Anhydrides are included.

Illustrative non-limiting examples of dopants suitable for use are: trifluoroacetic acid, difluoroacetic acid, perfluoropropionic acid, chlorodifluoroacetic acid, trifluoroacetic anhydride and perfluoropropionic anhydride. The preferred dopant is trifluoroacetic acid.

The liquid coating compositions suitably contain about 50-80% by wt. of a liquid or low-melting organotin carboxylate and about 20-50% by wt. of the fluorine dopant, which is either soluble in the organotin, capable of being solubilized by a third agent, or capable of being vaporized separately from the organotin compound. The preferred liquid coating compositions comprise about 50-60% of the organotin compound and about 40-50% by wt. of the fluorine dopant.

The fluorine-doped tin oxide coatings are deposited by chemical vapor deposition, preferably from a vaporized liquid coating composition; the compounds also can be vaporized separately in a heated chamber from about 100-300° C, preferably from 130-200° C.

A preheated carrier gas transports the vapor to a nozzle which disperses the vapors uniformly over a substrate, usually glass, heated to a temperature of about 450-750° C, preferably 600-700° C. The carrier gas may be air, oxygen, or nitrogen and its temperature can range from 100-300° C, preferably from 130-200° C. The flow rate of the carrier gas can range from 1-100 lit r/min, pref rably 25-75 liters/min, and its velocity can range from 0.25-5 m/sec, preferably from 0.5-3 m/sec. The concentration of the precursor in the carrier gas can range from about 0.1 to 10 mol%, pref rably from about 0.1-2 mol%.

Using the compositions and methods described it has be n found possible to prepare fluorine-doped tin oxide coatings having bulk resistivities <9 x 10^{-4} ohm-cm., haze values of <1% (Gardner Hazemeter), a visible transmittance of 80% or more, and an infrared reflectivity of >65%, for a coating thickness of 2000 Å.

Embodiments of the invention are now described by way of example.

EXAMPLE 1

a.) A liquid coating composition of 60 wt.% dibutyltin diacetate (DBTA) and 40 wt% trifluoroacetic acid (TFA) was injected via a syringe pump into a 170° C. air stream flowing at 70 liters/min. The concentration of the vaporized solution in air was 0.25 mol%. The vapor was transported to a soda lime silica glass substrate maintained at a temperature of 600° C. A transparent, conductive fluorine-doped tin oxide coating of about 1920 Å was deposited. The bulk resistivity was 6.3 x 10^{-4} ohm-cm. and the Gardner haze value was less then 1%. The sheet resistance of the film was 33 ohms/sq., as measured by a four-point probe.

b.) The effect on bulk resistivity of varying the concentration of trifluoroacetic acid in the liquid coating composition is shown in the following Table.

Table

Effect of Conc. of Trifluoroacetic Acid on Bulk Resistivity of Films	
Liquid Coating Composition (Wt%)	F-Doped Tin Oxide Film Bulk Resistivity
DBTA/TFA	(x 10^{-4} ohm-cm)
50/50	6.3
60/40	6.3
70/30	7.1
80/20	8.1
85/15	9.4
90/10	12.4
95/5	19.2

The results in the Table shown that the desired low bulk resistivities of 10^{-4} ohm-cm are achieved with a DBTA/TFA ratio of about 50:50 wt.%; relatively low TFA compositions, on the other hand, produce fluorine-doped tin oxide coatings having much poorer bulk resistivity values.

The preferred liquid coating compositions of the invention provide coatings which have low bulk resistivities and low haze values, at a relatively high tin content. These parameters are achieved herein preferably by using about 50-60% by wt. of DBTA and about 40-50% wt. of TFA.

The improved coatings obtained as described are made by chemical vapor deposition in the substantial absence of any solvent for the components of the composition., e.g. less than 10% by wt. of the composition.

Claims

1. A liquid coating composition comprising about 50-80% by weight of an organotin di- or tricarboxylate and about 20-50% by wt. of an organic fluoroacid.

2. A liquid coating composition according to claim 1 comprising about 50-60% by wt. of said organotin di-or tricarboxylate, and about 40-50% by wt. of said fluoroacid.

3. A liquid coating comp sition according to claim 1 or claim 2 wherein said organotin di-or tricarboxylate is of the formula

$R^1_xSn(0_2CR^{11})_{4-x}$

where R^1 is a C_1 to C_4 straight or branched chain alkyl or $R^{111}CH_2CH_2$ - where R^{111} is $R^{1V}0_2C$ or CH_3CO and R^{IV} is C_1 to C_4 alkyl; R^{11} is C_1 to C_4 straight or branched chain alkyl; and x is 1 or 2.

4. A liquid coating composition according to any one of claims 1 to 3, wherein said fluoroacid is selected from trifluoroacetic acid, difluoroacetic acid, perfluoropropionic acid, chlorodifluoracetic acid, trifluoroacetic anhydride and perfluoropropionic anhydride.

5. A liquid coating composition according to any one of the preceding claims wherein said organotin di- or tricarboxylate is selected from dibutyltin diacetate, butyltin triacetate, methyltin triacetyate, dimethyltin diacetate, dibutyltin dipropionate, dimethyltin dipropionate, methyltin tripropionate, diisobutyltin diacetate, bis(carbomethoxyethyl)tin diacetate, and bis(3-oxobutyl)tin diacetate.

6. A liquid coating composition according to any one of the preceding claims wherein said organotin di- or tricarboxylate is dibutyltin diacetate and said organic fluoroacid is trifluoroacetic acid.

7. A liquid coating composition according to claim 1 comprising about 60% by wt. dibutyltin diacetate and about 40% by wt. trifluoroacetic acid.

8. A liquid coating composition according to any one of the preceding claims, substantially solvent-free.

9. A method of forming a fluorine-doped tin oxide coating on glass, comprising applying a vaporised organotin di- or tri-carboxylate and a vaporised organic fluoroacid to the heated glass surface.

10. A method according to claim 9, comprising vaporising a composition according to any one of claims 1 to 8.

11. A method according to claim 9 wherein the organotin compound and fluoroacid are vaporised separately from one another.

12. A method according to any one of claims 9 to 11 wherein the glass surface is at a temperature of from 450-750 °C.

13. A fluorine-doped tin oxide coating on glass, obtainable by a method according to any one of claims 9 to 12.

14. A coating according to claim 13, having a bulk resistivity of 9×10^{-4} ohm.cm or less.

European Patent
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EUROPEAN SEARCH REPORT

Application Number

EP 89 30 8096

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	EP-A-0 186 481 (M & T CHEMICALS INC.) * Claims 1,4,9-10; page 5, lines 11-24 *	1-2,4,8-14	C 03 C 17/245
Y		3,5-7	
Y	FR-A-2 241 630 (RCA CORP.) * Claims; page 3, lines 24-29 *	1,3,5-7	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

C 03 C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	24-11-1989	BOUTRUCHE J.P.E.

CATEGORY OF CITED DOCUMENTS

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